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(54) Title: METHOD AND SYSTEM FOR MANUFACTURING DISPERSE COMPOSITE MATERIALS

(57) Abstract

The manufacturing of fine dispersed materials of the size form nanometers with a homogeneous interior and an additional coating is according to the invention realized by a plasma processing of high efficiency. These disperse composite materials (DCM) have specific properties of abrasion or wear resistance, friction, catalytic action or sintering e.g. for high temperature superconductors.

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METHOD AND SYSTEM FOR MANUFACTURING DISPERSE COMPOSITE MATERIALS

TECHNICAL FIELD

The invention relates to material manufacturing and, more particularly, to manufacturing disperse composite materials.

BACKGROUND OF THE INVENTION

In production of disperse catalysts one of the important problems is to produce catalytic coatings thin and strongly connected with an initial disperse material (carrier). It is especially necessary when expensive metals such as platinum, gold, iridium, palladium, or rhodium are used as catalytic active components of coatings since the coating has to have a strong adhesion to the carrier to provide a high life time of the catalyst.

In practice of creating new materials there is a wide use of various disperse composite materials on the base of diamonds, oxides, silicon silicates or nitrides, titanium, tungsten zirconium, vanadium, molybdenum, boron, aluminum etc., covered with shells of one or several metals: nickel, cobalt, silver, copper, molybdenum, tungsten, titanium, aluminum, tin, lead, zinc, zirconium, metals of the platinum group etc. These materials are used in the processes of depositing various (for example, strengthening, abrasive, abrasive resistant, heat resisting with no magnetic permeability, and also as a conductive phase in composite resistor) coatings upon the product as well as for creating high-strength structural composite materials.

Metallization of initial powders leads to the absence of contacts between the particles of the carrier material among themselves, i.e. to matrix structure of macroscopic compositions in the product. Besides the deposition of coatings, being diffusion barriers for atoms of initial powders, allows to suppress recrystallization during the process of manufacturing the product by sintering method. It opens a possibility of making the stable materials with a super small sized grain. Besides that the DCM can be used as an intermediate material during soldering or welding various

ceramic and other nonmetal items with metals, for example, as a solder for junction of high temperature superconductors (HTSC) of electrolytes with current leads. Coating material for this method can be, for example, silver, which is one of few metals not interacting with oxygen HTSC materials and used for treading low resistive contacts.

Among the requirements for DCM there is a high adhesion of coatings to the disperse carrier and controllability of the coating process necessary to take place under the given parameters of particle structure and content and leading to homogeneity of the produced powders.

All the hitherto known manufacturing methods for these materials have a number of shortcomings. These are: insufficient continuity of the obtained coating, poor adhesion of the deposited component to the particles of the initial material, formation of sinters, containing a few particles of an initial material inside the same shell that results in heterogeneity of the produced powders and, in the final analysis, in a strong degrading of the strength of the product, its wear resistance and applicability.

SUMMARY OF THE INVENTION

The invention overcomes the limitations of the prior art and provides additional benefits by providing methods and systems for manufacturing disperse composite materials. Aspects of the invention are directed to methods and apparatus for manufacturing of disperse composite materials (D.C. M.) by deposition of coatings on dust particles of at least 1 nm size such that the particles are injected as a dust plasma into a discharge plasma. The material for the coatings is supplied as gas or vapor into the discharge plasma for deposition on the surfaces of the particles.

Other aspects include working parameters of the system being in ranges with two or more steps or the first has the conditions of concentration $n_k < n(T)$ and the second or the following steps have concentrations of the components of fulfilled by the condition $n_k > n(T)$. Further aspects included be the DCM coatings being produced as

host metals for simultaneous or subsequent loading with high concentrations of hydrogen or its isotopes for low energy nuclear transmutations.

DETAILED DESCRIPTION OF THE INVENTION

The invention refers to chemistry, metallurgy, material sciences and micro-technology for manufacturing disperse composite materials as powders which consist of small particles and which are covered with another material. These dispersed composite materials (DCM) can be produced as catalysts, as abrasive, wear-resistant grinding material of high strength of with surfaces without magnetic permeability. A further use of the composite materials applies the structural properties of very small size particles of very high strength as these are needed for composite resistors, or during the process of soldering or welding of ceramic materials (high temperature superconductors, rigid electrolytes etc.) with metals.

The difficulties of the hitherto known methods are overcome according to the invention described in the following systems and method where - according to the invention - the deposition process is essentially better controlled and the exactness of the deposition process of the coating components onto the fine dispersed basic material is performed. Accordingly the sintering of the carrier material is avoided during the process of deposition of the covers and simultaneously the adhesion of the cover on the carrier is improved.

The system and the method for producing the DCMs consists in filling of a working chamber with a plasma producing gas which is being excited to plasma, and in injection of the dispersed (dusty) base material as well as the one or other components of the coating material being in the gas or vapor phase. According to the invention, the working conditions for the generation of the coatings are

$$[33{,}6kT/(\varepsilon_o 1_d^2 \phi^2)]^3 < n_d < en_i/(1_d 2\pi\varepsilon_o \phi) \qquad (1)$$

where n_d is the average density of the dust particles in the plasma in m^{-3}, k is the Boltzmann constant in J/K, T is the temperature of the plasma producing gas K, εo is the electric (influence) constant in F/m, l_d the average size of the dust particles in m, e is the charge of the electron in C, n_i the ion concentration in the generated gaseous plasma, and ϕ is the floating potential, in V, of the dust particles in the plasma fulfilling the condition

$$\phi > 1{,}5\ V \tag{2}$$

and the concentration n_k in m^{-3} of the components in the plasma follows the condition

$$n_k < n(T) \tag{3}$$

where n(T) is the concentration of the components in m^{-3} at the saturation pressure of the gas pressure of the components at a temperature T in K.

This just describe method is being modified in the presence of a gravitation field with a gravitation acceleration g in m/s^2 within the reaction chamber by the an electric field whose field strength E (in V/m) is given by

$$E > l_d^2 \rho_d g/(12\varepsilon_o\phi) \tag{4}$$

where ρ_d is the density of the dust particles (of the base material) and the direction of the electric field E is the same as the that of the gravitation force.

A further modification of the working parameters against the equations (1) and (4) is given by the average concentration of the dust particles in the plasma

$$n_d < 2en_kD_k\phi\xi\mu_k/(RTKl_d\rho_s\delta_s);\ K=K_o\lambda\exp(-\lambda);\ \lambda=\pi\phi\varepsilon_o l_d/(kT) \tag{5}$$

where D_k is the diffusions constant of one component in the plasma in m^2/s, m_s is the molecular weight of one component in kg/mol, ξ is the share of the sintered particles in the final product; K_o is the coagulation constant of the particles in the gas m^3/s, ρ_S is the density of the coating material in kg/m^3, R is the universal gas constant in J/(mol-K), and l_d is the thickness of the coating in m.

Furthermore the following modification can be used for the working conditions (1) and (4) according to the invention: the process for the incorporation of the components into the plasma is being performed within at least two steps, where the first steps fulfills the condition

$$n_k < n(T)$$

and the following steps fulfill the condition

$$n_k > n(T)$$

In the plasma the dispersed particles are charged negatively essentially as it is known form the theory of double layers (S. Eliezer, and h. Hora, Physics Reports, 172, 339 (1989)) and is due to the fact that the electron mobility considerably exceed the ion one. The characteristic time for charging the dust particles is within 0.1 to 0.01 ms. The magnitude of the stationary charge of the dust particles and their floating potential are determined by a condition of equality of electron and ion flow in a particle. When an additional gaseous or vapor component is injected it is ionized with formation of positive ions and electrons. In a field of Coulomb forces of charged particles, the positively charged ions are attracted to dusty particles, are deposited there, and form the coating whose thickness is determined by the component concentration of the added plasma forming gas and by the exposure time. To coat the dust particle they have to be separated each other to be in such condition for a long period of time. The space

separation of the particles takes place due to their rather large electric charge of the same sign. In the same electrostatic way the dust particles are kept off the walls of the working chamber. This mutual repulsion of the dust particles is leading to a long living quasi crystalline structure and prevents the coagulation.

For satisfying the working conditions (1), the ordered state of the small particles is being produces as a dust plasma. The generation of the quasi crystalline state permits the addition of the one or the other vapor or gaseous components to cover the dust particles with carefully defined - including complicated - coatings for manufacturing the desired DCMs.

The coating which is being produced with this process of deposition of ion, has an especially high strength of adhesion, In the considered case of the energy of a deposited ion should be comparable with or greater then the sorption energy of admixture atoms adsorbed on a surface. The sorption energy of the majority of atoms is < 1.5 eV. Therefore, the minimum of the floating potential ϕ has to exceed 1.5 V. It is well known that the plasma generating gas ions during this process of the removing of small plasma surfaces fulfills the same condition.

It should be noted that if during deposition the coating, the condition $n_k <$ n(T) is satisfied. The coating grows atom by atom and forms a dense shell on a particle. If $n_i >$ n(T) the vapor becomes over saturated and in it there can be liquid or dense clusters of the introduced component atoms. In this case the formation of the coating may develop a dendrite structure.

The given value of ϕ permits an estimation of the concentration n_d of the added dust particles. For a value of $l_d = 10^{-6}$m, ϕ=1,5V, T=300K, $n_i = 10^{16}m^{-3}$, the condition of the density of the dust particles is $3{,}5 \cdot 10^{11}\ m^{-3} < n_d < 3 \cdot 10^{13}\ m^{-3}$.

Inequality (1) leads to the lower limit of l_d for a given ϕ, if an arbitrary value of n_d is chosen. In the case described in the preceding paragraph, the working parameter is the minimum of $(l_d)min = 4.5 \cdot 10^{-7}$ m.

Without loss of generality zero-gravity was assumed. In the presence of a gravitation field this can be compensated in the working chamber by an electric field E for negatively charged particles The magnitude of this field is determined by the condition of equilibrium according to equation (4). If $l_d=10^{-6}$m, ϕ=1.5V und $r_d=3.5\cdot10^3$ kg/m^3, the working parameter is E>2 16 V/m.

ON of the main advantages of the quasi crystalline state of the dust particles for the deposition of the coatings is the levitation of the particles without mutual touching. During the process the dust particles are being coated without that two or more particles are sintering together. This condition for generation of a periodic structure is rather rigorous, requires rather high concentration of particles and results in a restriction to smaller size particles. These restriction can - according to the invention - be overcome partially and the smallest size of particles can be decreased essentially is the effect of suppression of the coagulation in the dust plasma is used. The condition for the exposure time τ for producing a required thickness δ_s of the coating is less than the characteristic time for the period t_ξ during which the concentration of the particles arrives at a value ξn_d due to the sintering process, as can be determined by equation (5). At this in condition sintering in the final products appears for two or more particles within the same coating but their part does not exceed the given magnitude ξ.

As an application of the invention, the example for producing diamond particles with a nickel coating as DCM will be described.

The discharge chamber is cylindrical of 10 cm diameter and 50 cm high (Distance of the electrodes) being filled, as an example, with argon as plasma generating gas. The plasma is being excited and the concentration of ions and electrons is taken at a level of n_i of about 10^{17} m^{-3} at a temperature of T = 1273K (1000°K) where the characteristic field strength is E = 650 V/m. The portion of the before dispersed dust particles of a density ρ_d=3510 kg/m^3 with an average size of l_d of about 2µm an a total amount of about $2x10^{10}$ dust particles arrives at an average concentration of n_d = $5x10^{12}$m^{-3} where the floating potential in the plasma has to be kept at 2 eV. Then the

nickel vapor is introduced with a concentration n_k of about $1{,}7x10^{15}m^{-3}$. The exposure time is 16 seconds for producing a monatomic layer of 0.3 nm thickness. The introduction of the nickel vapor is being performed by nickel metal at a temperature of T=1273K in the plasma where a saturated partial pressure of the nickel vapor is created at the conditions of the working parameters. The generated nickel as has an exceedingly high abrasion resistivity.

As a further example, the manufacturing of a disperse platinum catalyst is given.

The discharge chamber of a cylindrical form with an internal diameter of d=0.1 m and a height (distance between the electrodes) h=0.5m is filled with a plasma forming gas, for example argon. The plasma is then excited. The concentration of the ions and electrons are maintained at a level of about $10^{17}m^{-3}$ with a temperature T at 1673K (1400°C), and electrical field strength is maintained at a level of E=14800 V/m. The portion of the before dispersed dust particles of Al_2O_3 (density 3960 kg/m^3) and an average diameter of 10 μm and a total number of about $7.9x10^9$ to provide an averaged concentration equal to $2x10^{12}$ m^{-3} is introduced into the plasma. A floating potential of ϕ = 2.5 eV is maintained. Then the first stage of introducing platinum vapor is performed with a platinum concentration at the level $5x10^{14}m^{-3}$ corresponding to the saturation vapor pressure of platinum at the mentioned temperature. The exposure time is 135 seconds resulting in a monatomic layer of 0.3 nm thickness coating the initial dust particles, where the performed coating is dense under these conditions.

The second stage of introducing platinum vapor into the plasma is performed by heating up the vapor sources to a temperature of 1773K (1500°C) which leads to a corresponding vapor concentration of about $n_i = 4.2x10^{15}m^{-3}$. At working conditions (T=1673K), this vapor becomes over saturated and that results in the formation of clusters consisting in several platinum atoms. Under these conditions an exposure time of about 160 seconds the thickness of about ten atomic layers (3 nm) of particles is in the coating. At these conditions the coating is not only performed by a

sedimentation process of atoms but also by that of dense liquid platinum clusters, Further removing the produced particles from the reaction zone is performed by short term decrease of the electric field strength.

A further example is from manufacturing of high temperature superconducting material.

The same cylindrical with argon filling and plasma excitation is used as before. The electron and ion concentration is being kept at a level of $n_i = 10^{18}m^{-3}$ with a temperature of 1674K (1400°C) and an electric field of 19.6 kV/m. The initially dispersed $YBa_2Cu_3O_7$ particles of about 10 μm size and 5300 kg/m^3 density have a total number of $4x10^{10}$ and an average concentration of $n_d = 1.2x10^{17}m^{-3}$. The floating potential ϕ is 2.5 V. In the first stage, silver vapor is acting for 10 seconds for a pre-deposition of the high temperature superconducting particles and to remove adsorbed contamination. Then the silver is heated to 1023K (750°C) according to a saturated vapor concentration of $n_k = 1.2x10^{17}m^{-3}$. At the working conditions of T=600K, the vapor is strongly saturated leading to clusters of silver atoms. At an exposure time of 30 seconds, coatings are produced which correspond to the fraction of total mass in the final product of 1% due to the condensation of the silver clusters. Further removing of the produced particles from the reaction zone is performed by short-term decrease of the electric field strength. The items made of the materials have a very high mechanical strength

A special application of this method and apparatus is the manufacturing of coatings which leads to a very low cost conversion of long lived radio nuclides (mostly form nuclear reactors) into stable nuclides or the elimination of plutonium by transmutation into uranium. It is well known that nuclear reactions in host metals (nickel, palladium, titanium, zirconium, thorium, etc.) for high concentrations of hydrogen ions of its isotopes are used which are occurring as low energy long time processes in nuclear distances in the range of picometers (H. Hora et al. Transactions of the American Nuclear Society, 766, 144 (1997)). It is essential that very high surfaces

with multilayers of appropriate host metals are made as it is done according to the invention with the DCMs. The material added to the plasma for production of the coatings (on glass or similar carrier materials of the size around 10 μm) is then one or in a sequence further mentioned host metals as well as charges of the long time radio nuclides for transmutation, preferably into the surfaces or in interfaces.

CLAIMS

It is claimed:

1. A system for manufacturing disperse composite materials (DCM) by deposition of coatings on surfaces of dust particles, the system comprising:

a discharge plasma;

an injector configured to inject the dust particles into the discharge plasma; and

coating material being either a gas or a vapor, the coating material being introduced into the discharge plasma for deposition on the surfaces of the particles.

2. The system of claim 1, wherein parameters of the system are in accordance with the relation $[33,6kT/(\varepsilon_o 1_d^2 \phi^2)]^3 < n_d < en_i/(l_d 2\pi\varepsilon_o \phi)$.

3. The system of claim 1, wherein parameters of the system are in accordance with the relation $E > l_d^2 \rho_d g/(12\varepsilon_o \phi)$.

4. The system of claim 1, wherein parameters of the system are in accordance with the relations $n_d < 2en_k D_k \phi \xi \mu_k/(RTKl_d \rho_s \delta_s)$ and $K=K_o \lambda \exp(-\lambda)$; $\lambda=\pi\phi\varepsilon_o l_d/(kT)$.

5. The system of claim 1, wherein parameters of the system are in ranges having at least two steps, the first step having the conditions of concentration $n_k < n(T)$ and the second or following steps having concentrations of the components fulfilling the conditions $n_k > n(T)$.

6. The system of claim 1 further comprising a hydrogen loader configured to load a high concentration of hydrogen or its isotopes with the DCM coatings either simultaneously or subsequently to the production of the DCM coatings, the DCM coatings being host metals for the loading of the hydrogen or its isotopes.

7. The system of claim 6 wherein the DCM coatings of host metals for simultaneous or subsequent loading with high concentrations of hydrogen or of its isotopes are produced with additional nuclides for low energy nuclear transmutations.

8. The system of claim 1 wherein the dust particles are at least 1 nm in size.

9. A method for manufacturing disperse composite materials (DCM) by deposition of coatings on dust particles, the method comprising:

creating a discharge plasma;

injecting dust particles into the discharge plasma;

introducing coating material as a gas or vapor into the discharge plasma for deposition on the surfaces of the particles.

10. The method of claim 9, wherein parameters of the method are in accordance with the relation $[33,6kT/(\varepsilon_o l_d^2 \phi^2)]^3 < n_d < en_i/(l_d 2\pi\varepsilon_o \phi)$.

11. The method of claim 9, wherein parameters of the method are in accordance with the relation $E > l_d^2 \rho_d g/(12\varepsilon_o \phi)$.

12. The method of claim 9, wherein parameters of the method are in accordance with the relations $n_d < 2en_k D_k \phi \xi \mu_k/(RTKl_d \rho_s \delta_s)$ and $K=K_o \lambda \exp(-\lambda)$; $\lambda=\pi\phi\varepsilon_o l_d/(kT)$.

13. The method of claim 9, wherein parameters of the method are in ranges having at least two steps, the first step having the conditions of concentration $n_k < n(T)$ and the second or following steps having concentrations of the components fulfilling the conditions $n_k > n(T)$.

14. The method of claim 9 further comprising loading a high concentration of hydrogen or its isotopes with the DCM coatings either simultaneously or subsequently to

the production of the DCM coatings, the DCM coatings being host metals for the loading of the hydrogen or its isotopes.

15. The system of claim 9 wherein the DCM coatings of host metals for simultaneous or subsequent loading with high concentrations of hydrogen or of its isotopes are produced with additional nuclides for low energy nuclear transmutations.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C23C 16/00.
US CL :118/716, 723 R

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 118/716, 723 R, 715.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, X	US 5,846,600 A (YAMADA et al) 08 December 1998, column 10 line 11 through col 12 line 47.	1-15
A	US 5,593,740 A (STRUMBAN et al) 14 January 1997, entire document.	1-15

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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